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METHOD FOR MANUFACTURING ENHANCED POLYETHYLENE GROUP
RESIN PRE-FOAMED PARTICLES
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Specification

1. Title of the invention

Method for Manufacturing Enhanced Polyethylene Group
Resin Pre-Foamed Particles

2. Claims

1. A method for manufacturing enhanced polyethylene group resin pre-foamed particles, characterized by the fact that polyethylene group resin particles at 100 parts by weight, a vinyl aromatic monomer at 5-300 parts by weight, and a polymerization initiator at 1.0-3.0 parts by weight to said monomer are dispersed into an aqueous medium and heated to a temperature at which the polymerization of said monomer is not substantially caused, so that said monomer is impregnated in the above-mentioned polyethylene group resin particles and on the surface; and after the temperature of the above-mentioned aqueous suspension is raised, said monomer is polymerized and foamed by

¹ Numbers in the margin indicate pagination in the foreign text.

impregnating a volatile foaming agent during the polymerization or after finishing the polymerization.

2. The manufacturing method of Claim 1, characterized by the fact that the vinyl aromatic monomer is 30-200 parts by weight to the polyethylene group resin particles at 100 parts by weight.

3. The manufacturing method of Claim 1, characterized by the fact that the polymerization initiator is 1.1-2.0 parts by weight to the vinyl aromatic monomer at 100 parts by weight.

3. Detailed explanation of the invention

(Industrial application field)

The present invention pertains to a method for manufacturing enhanced polyethylene group resin pre-foamed particles. More specifically, the present invention pertains to a method for manufacturing enhanced polyethylene group resin pre-coated particles that render a foamed molded body with very excellent rigidity and impact resistance.

(Prior art)

In general, the foamed body of a polyethylene group resin also has merits of excellent oil resistance and impact resistance in addition to its high elasticity and

large strain recovery force to a repeated stress and is broadly utilized as an important packing material. However, in case a foamed molded body is obtained by changing the polyethylene group resin particles to pre-foamed particles and molding them in a mold, the pre-foamed particles and the foamed molded body after molding in the mold are easily contracted due to the low rigidity of the polyethylene, the foamed molded body obtained is soft and has a low compressive strength as demerits. /2

As a method for improving these drawbacks, methods for obtaining enhanced polyethylene group resin pre-foamed particles by impregnating the polyethylene resin with a vinyl aromatic monomer and polymerizing them are proposed by Japanese Kokoku Patent Nos. Sho 45[1970]-32623, Sho 51[1976]-46138, Sho 52[1977]-10150, Sho 59[1984]-3487, etc. However, in these methods, since the impregnation of the vinyl aromatic monomer into the polyethylene group resin and the polymerization are simultaneously carried out in parallel, a nonuniformity is caused in the polymerization reaction on the surface of the particles and in the particles, so that the homogeneity of the particles generated is inferior, and a non-negligible amount of said monomer is polymerized as single particles before being impregnated in the polyethylene group resin.

In order to solve these problems, in Japanese Kokoku Patent Nos. Sho 58[1983]-53003, Sho 58[1983]-51009, and Sho 58[1983]-51010, a method that impregnates a vinyl monomer and a polymerization initiator at 0.01-0.3 part by weight to said monomer at 100 parts by weight in polyethylene group resin particles by 80% or more of said monomer at a temperature, at which the polymerization initiator is not substantially decomposed, and polymerizes them by raising the temperature is presented. According to this method, it is described that with the separation of the impregnating process and the polymerizing process, the homogeneity of the particles generated are improved and a homopolymer of the vinyl group monomer is not generated in actuality. (Problems to be solved by the invention)

The particles being obtained by impregnating and polymerizing the vinyl group monomer with the polyethylene group resin particles as mentioned above have a sea-island structure in which the vinyl group polymer particles are dispersed into the matrix of the polyethylene group resin. However, according to the above-mentioned prior arts, the dispersed particle diameter of the vinyl group polymer is large, and the foamed molded body being obtained by pre-foaming said generated particles and further heating and

molding them is not satisfactory in both the rigidity and the impact resistance.

(Means to solve the problems)

The purpose of the present invention is to manufacture enhanced polyethylene group resin pre-foamed particles for rendering a foamed molded body that has excellent impact resistance, which is a property intrinsic to a polyethylene group resin, and improved rigidity. The present invention provides a method for manufacturing enhanced polyethylene group pre-foamed particles that render a molded product with excellent impact resistance and rigidity by decreasing the dispersed particle diameter of a vinyl aromatic polymer in the particles generated by using the amount of polymerization initiator at 0.1-3.0 parts by weight, which can polymerize the vinyl aromatic monomer, to said monomer at 100 parts by weight.

In other words, the present invention provides a method for manufacturing enhanced polyethylene group resin pre-foamed particles characterized by the fact that polyethylene group resin particles at 100 parts by weight, a vinyl aromatic monomer at 5-300 parts by weight, and a polymerization initiator at 1.0-3.0 parts by weight to said monomer are dispersed into an aqueous medium and heated to a temperature at which the polymerization of said monomer

is not substantially caused, so that said monomer is impregnated in the above-mentioned polyethylene group resin particles and on the surface; and after the temperature of the above-mentioned aqueous suspension is raised, said monomer is polymerized and foamed by impregnating a volatile foaming agent during the polymerization or after finishing the polymerization.

As the polyethylene group resin being used in the present invention, low-density polyethylene, straight-chain low-density polyethylene, high-density polyethylene, ethylene/propylene copolymer, ethylenepropylene/butene-1 copolymer, ethylene/vinyl acetate copolymer, ethylene/acrylic acid copolymer, ethylene/vinyl chloride copolymer, and blends of two kinds or more of them are mentioned. As the above-mentioned straight-chain low-density polyethylene, a copolymer of ethylene and α -olefin is preferable. As the α -olefin, for example, 1-butene, 1-pentene, 1-hexene, 3,3-dimethyl-1-butene, 4-methyl-1-pentene, 4,4-dimethyl-1-pentene, 1-octene, etc., are mentioned. These polyethylene group resins may also be crosslinked. Its average molecular weight is appropriately in a range of about 0.05-5 mm. If the average particle diameter is smaller than 0.05 mm, the dissipation of the foaming agent is severe. Also, if large particles of

greater than 5 mm are used, the dispersion during the polymerization is difficult, and the filling characteristic during the molding is poor, which is not preferable.

As the vinyl aromatic monomer being used in the present invention, nuclei-substituted styrene such as methylstyrene, dimethylstyrene, isopropylstyrene, and chlorostyrene in addition to styrene, α -substituted /3 styrene such as α -methylstyrene, etc., are used alone or as a mixture of two kinds or more, or a mixture with a small amount of other monomers copolymerizable with the above-mentioned monomer, for example, acrylonitrile, acrylic ester, methacrylic acid ester, divinylbenzene, mono- or dialkyl maleate, and others is used.

The amount of vinyl aromatic monomer is 5-300 parts by weight, preferably 30-200 parts by weight to the polyethylene group resin at 100 parts by weight. If the amount is more than 300 parts by weight, the vinyl aromatic monomer is not uniformly, entirely absorbed by the polyethylene group resin, and the monomer that is not absorbed is polymerized alone, which is not preferable. Also, the polyethylene group resin that has absorbed a large amount of vinyl aromatic monomer loses the properties intrinsic to the polyethylene. On the other hand, if the amount of vinyl aromatic monomer is less than 5 parts by

weight, the improvement of the rigidity of the polyethylene group resin is not sufficient, which is not preferable.

As the polymerization initiator being used in the present invention, generally, substances being used as initiators for the suspension polymerization of the vinyl aromatic monomer can be used as they are. For example, there are organoperoxides such as benzoyl peroxide, lauroyl peroxide, t-butyl peroxide, t-butyl peroxybenzoate, 1,1-bis(t-butylperoxy) 3,3,5-trimethylcyclohexane, t-butylperoxyisopropyl carbonate, 2,2-bis(t-butylperoxy)butane, and dicumyl peroxide; azo compounds such as azoisobutyronitrile and azobisdimethylvaleronitrile, etc. These polymerization initiators may be used alone or in combination of two kinds or more. The polymerization initiator should be soluble in an oil, is dissolved in the vinyl aromatic monomer or dissolved in a small amount of solvent, which does not cause an obstacle to the polymerization reaction, for example, toluene, and added simultaneously with the vinyl aromatic monomer or separately into an aqueous medium. The amount of polymerization initiator being used is 1.0-3.0 parts by weight, preferably 1.1-2.0 parts by weight to the vinyl aromatic monomer at 100 parts by weight. If the amount is less than 1.0 part by weight, the dispersed

particle diameter of the vinyl aromatic polymer in the enhanced polyethylene group resin particles being obtained is large, and in the foamed molded body being obtained by pre-foaming said particles and further heating and molding them, not only its rigidity is not improved, but the impact resistance intrinsic to the polyethylene group resin is damaged. Even if the polymerization initiator is used at more than 3.0 parts by weight, the molecular weight of the vinyl aromatic polymer is not decreased more than is necessary, which is not preferable.

With the control of the amount of polymerization initiator to 1.0-3.0 parts by weight, the dispersed particle diameter of the vinyl aromatic polymer in the polymerized particles generated is decreased, a fixed or more molecular weight can be maintained, and the rigidity and the impact resistance of the foamed molded body can be markedly improved.

As the suspension being used in the present invention, water-soluble high-molecular substances such as polyvinyl alcohol, polyvinylpyrrolidone, and methyl cellulose; slightly soluble inorganic substances such as calcium phosphate, magnesium pyrophosphate, and magnesium oxide, and the like can be used.

The vinyl aromatic monomer is impregnated by heating under the condition in which said monomer is not substantially polymerized. A higher impregnation temperature is preferable in terms of impregnation stimulation, however since the vinyl aromatic monomer before impregnating is polymerized by a too early decomposition of the polymerization initiator, an appropriate temperature setup is required. A weight increase portion after immersing a polyethylene group resin with a known weight into a large amount of vinyl aromatic monomer is set to a saturated amount being impregnated at the temperature and measured at a certain temperature, so that the impregnation time is appropriately about 30 min-3 h.

After impregnating the vinyl aromatic monomer, the vinyl aromatic monomer is polymerized while stirring by raising the temperature of the aqueous suspension again. Under the temperature at which the polymerization initiator is sufficiently decomposed, the polymerization time is generally 3-20 h.

The foaming agent being used in the present invention has a property that does not dissolve the generated enhanced polyethylene group resin particles or only slightly swells the particles, and substances that are

gaseous or liquid at normal temperature and normal pressure are used. For example, there are aliphatic hydrocarbon resins such as n-propane, n-butane, isobutene, n-pentane, isopentane, neopentane, n-hexane, and isohexane, alicyclic hydrocarbons such as cyclobutane and cyclopentane, and $\frac{1}{4}$ halogenated hydrocarbons such as methyl chloride, ethyl chloride, methylene chloride, trichlorofluoromethane, dichlorofluoromethane, dichlorodifluoromethane, chlorodifluoromethane, and dichlorotetrafluoroethane, and they can be used alone or by mixing two kinds or more.

As the method for pre-foaming the enhanced polyethylene group resin particles obtained as mentioned above, any of a method using vapor as a well-known technique and methods proposed in West German Laid-Open Patent No. 2,107,683, Japanese Kokoku Patent No. Sho 56[1981]-1344, etc., may be employed. For example, in the method of Japanese Kokoku Patent No. Sho 56[1981]-1344, generated particles are dispersed into an aqueous medium in the presence of a volatile foaming agent and a suspension in a pressure-resistant container and heated in this state, and the volatile foaming agent is impregnated into the particles and heated to a softening temperature or higher of said particles under pressurization of a vapor pressure or higher of the volatile foaming agent. In this state,

while constantly maintaining the internal pressure of said pressure-resistant container, both said particles and water are discharged to a low-pressure region from said pressure-resistant container.

(Operation and effects)

In the present invention, as mentioned above, a polymerization initiator that can polymerize a vinyl aromatic monomer is used at 1.0-3.0 parts by weight to said monomer, so that the dispersed particle diameter of the vinyl aromatic polymer existing in the resin particles generated after polymerizing is set to 0.05-1.0 μm , which is a micro-dispersion up to about 1/10 of the particle diameter of the prior art. Needless to say, this level cannot be achieved at all by a simple blend.

The enhanced polyethylene group resin pre-foamed particles manufactured by the present invention is filled in a mold that can close the chains but cannot seal them, heated, and molded, so that a foamed molded body is obtained. This foamed molded body has higher rigidity and excellent impact resistance, compared with a polyethylene group resin foamed molded body enhanced by the conventional vinyl aromatic group, and is appropriately used in buffer materials, packing materials, containers, etc.

(Application examples)

Next, the present invention is explained by application examples, however the present invention is not limited to them.

Application Examples 1-5 and Comparative Examples 1-4

Pure water at 400 parts by weight, straight-chain low-density polyethylene resin particles with a density of 0.93 g/cm³ and a MFR of 2.1 g/10 min (made by Mitsui Petrochemical Industries, Ltd. "Ultozex 3021F") at 100 parts by weight, soda α -olefinsulfonate at 0.1 part by weight as a suspension, tricalcium phosphate at 3 parts by weight, and 1,1-bis(t-butylperoxy)3,3,5-trimethylcyclohexane at an amount shown in Table 1 as a polymerization initiator were dissolved in a styrene monomer at an amount shown in Table 1, added to an autoclave with an inner volume of 3.5 L, and stirred, so that an aqueous suspension was obtained.

Next, this aqueous suspension was held at an impregnation temperature of the styrene monomer and the polymerization initiator shown in Table 1 for 1 h, and the styrene monomer and the polymerization initiator were impregnated into the polyethylene resin particles.

Next, the temperature of this aqueous suspension was raised to 115°C, and said temperature was held for 4 h, so that the polymerization was completed.

After cooling the polymerized product down to 70°C, butane (75% n-butane and 25% isobutene) at 30 parts by weight was pressed into it, held at said temperature for 1 h, and cooled, and the resin particles were drawn out, washed with an acid, washed with water, and dried.

The foaming particles obtained were foamed in vapor and filled into a mold of 300 x 170 x 40 mm having many small holes that could close the chains but could not seal them, and vapor at a pressure of 1.0 kgf/cm² was injected from the small holes. After heating for 40 sec, the particles were cooled for 90 sec and drawn out.

The density, the degree of fusion, the compressive strength, and the Sharpy impact values of the foamed molded bodies obtained are shown in Table 1.

Application Examples 6-8 and Comparative Examples 5-7

The amount of said polymerization initiator and the amount of styrene monomer were set as shown in Table 1, and the polymerization was carried out similarly to the above-mentioned application examples and comparative examples until it was completed. Then, the polymerized product was cooled down to 60°C, and dichlorodifluoromethane at 50 parts

by weight was pressed into it. Then, the temperature was raised and held at 130°C. Next, while holding the internal pressure at 30 kgf/cm² by N², one end of the container was opened, and foaming was carried out. The pre-foamed particles obtained were molded similarly to the above application examples and comparative examples. The properties of the foamed molded bodies obtained were evaluated, and the results are shown in Table 1.

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Table 1

		发泡材料 粒子/发泡 母 体 (重量比)	发泡材料及 发泡母体 の混合 濃度 (%)	混合開始時 の 温度 (°C)	予備発泡 粒子倍率	発泡密度 (g/cm ³)	発 泡 体 性 質		
							50%圧 縮強度	400V- 衝撃値	融着度
実 施 例	1	100/10	4.0	1.1	4.0	2.3	1.9	2.8	○
	2	100/100	8.8	1.1	4.0	2.2	2.3	1.4	○
	3	100/100	8.5	2.5	4.0	2.3	2.2	1.4	○
	4	100/150	9.8	1.1	5.0	1.9	2.4	1.2	◎
	5	100/200	9.5	1.1	5.0	2.0	2.5	1.0	◎
	6	100/100	8.5	1.1	3.5	2.1	2.6	1.5	○
	7	100/150	9.0	1.1	4.5	2.1	2.3	1.2	○
	8	100/300	9.5	1.1	4.5	2.1	2.4	1.0	◎
比 較 例	1	100/100	8.5	0.4	4.8	2.0	1.7	0.8	△
	2	100/100	8.0	0.8	4.2	2.3	1.8	0.9	○
	3	100/100	8.5	3.2	3.8	2.5	1.3	0.8	×
	4	100/350	9.8	1.1	5.0	2.8	2.8	0.4	○
	5	100/100	8.5	0.4	4.0	2.4	1.9	2.7	△
	6	100/100	8.5	0.8	3.8	2.5	2.0	2.8	○
	7	100/100	8.5	1.2	3.5	2.8	2.0	2.4	×
	8	100/100	8.5	1.2	3.5	2.8	2.0	2.4	×

1. Polyethylene resin particles/styrene monomer (weight ratio)
2. Impregnation temperature (°C) of styrene monomer and polymerization initiator
3. Number of part of polymerization initiator (part by weight)
4. Pre-foamed particle magnitude
5. Foamed molded body density (g/L)
6. Foamed molded product property
7. 50% compressive strength
8. Sharpy impact value
9. Degree of fusion
10. Application Example
11. Comparative Example

(Note) (1) 50% compressive strength: /6

It was measured according to the JIS K 6767 method.

(2) Sharpy impact value:

A specimen (without a notch) of 20 x 30 x 150 mm was measured by a Sharpy tester set to a hammer weight of 20 kg, a hammer angle of 124°, and a span of 90 mm.

(3) Degree of fusion:

When the molded body was fractured by pulling out, the degree of fusion was decided by the fracture state of the fractured surface.

Ø: The particle surface exposure was less than 10%.

O: " was 10% to less than 40%.

Δ: " was 40% to less than 70%.

X: " was 70% or more.